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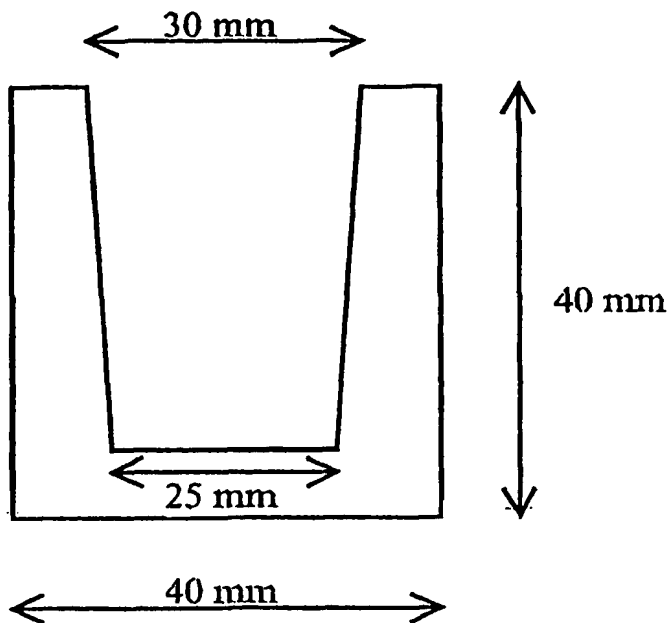
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(54) Title: MOULD PARTS OF SILICON NITRIDE AND METHOD FOR PRODUCING SUCH MOULD PARTS



(57) Abstract: The present invention relates to silicon nitride mould parts, particularly crucibles for use in connection with directional solidification and pulling of silicon single crystals. The mould parts consist of  $\text{Si}_3\text{N}_4$  having a total open porosity between 40 and 60% by volume and where more than 50% of the pores in the surface of the mould parts have a size which is larger than the means size of the  $\text{Si}_3\text{N}_4$  particles. The invention further relates to a method for producing the silicon nitride mould parts.

**Title of invention**

Mould parts of silicon nitride and method for producing such mould parts.

**5 Field of invention**

The present invention relates to mould parts of silicon nitride for use in connection with molten metal, particularly molten silicon, and to a method for producing such mould parts.

**10 Background art**

It is known to use quartz crucibles during crystallising of pure molten silicon by directional solidification and by crystal pulling from pure molten silicon. Quartz crucibles have, however, the drawback that quartz is wet by molten silicon, and solidified silicon will thereby affix to the walls in the quartz crucibles.

15 Further, quartz and silicon have different coefficients of thermal expansion, resulting in that when molten silicon solidifies in a quartz crucible, thermal stress will be introduced in the quartz crucible which will destroy the crucible. Quartz crucibles can therefore only be used once.

20 From JP-59-62199 it is known a method for the production of silicon nitride crucibles for use in pulling silicon crystals. The crucible according to JP-59-62199 can be produced by forming silicon powder by cold pressing, whereafter the crucible is heated in an inert atmosphere in a first step and thereafter nitridation is carried out at a higher temperature in a second step.

25 According to JP-59-62199 the produced crucibles have a density of 85% of the theoretical density for silicon nitride.

The crucibles according to JP-59-62199 have a good strength, but are wet by molten silicon to such an extent that the solidified silicon ingot sticks to the  
30 walls in the crucible. The ingot can thus not be removed from the crucible without destroying the crucible. The crucibles according to JP-59-62199 can thus only be used once when they are used for directional solidification of silicon. The same is true also when the crucibles according to JP-59-62199 are used for crystal pulling of silicon single crystals.

**Description of Invention**

The object of the present invention is to provide silicon nitride mould parts, such as crucibles, which are not wet by molten silicon thus avoiding that molten silicon which is solidified in the crucibles sticks to the wall of the  
5 crucible.

The present invention thus relates to silicon nitride mould parts, particularly crucibles for use in connections with directional solidification and pulling of silicon single crystals, which mould parts consist of  $\text{Si}_3\text{N}_4$  having a total open  
10 porosity between 40 and 60% by volume and where more than 50% of the pores in the surface of the mould parts have a size which is larger than the mean size of the  $\text{Si}_3\text{N}_4$  particles.

According to a preferred embodiment the mould parts are coated with silicon  
15 nitride particles having an average particle size of less than  $50\mu\text{m}$ .

It has surprisingly by been found that  $\text{Si}_3\text{N}_4$  mould parts having such an open porosity are not wet by molten silicon and have a strength making it possible to reuse the crucibles a number of times for directional solidification of molten  
20 silicon.

According to another aspect, the present invention relates to a method for the production of silicon nitride mould parts, particularly crucibles for use in connection with directional solidification of silicon, where particulate silicon  
25 having a particulate size of less then  $100\mu\text{m}$  is formed to a mould part and subjected to nitridation for conversion of the silicon particles to  $\text{Si}_3\text{N}_4$ , which method is characterized in that the forming is carried out under such a pressure and with such a particle size distribution of the silicon particles that the finished silicon nitride mould part has an open porosity between 40 and  
30 60% by volume. Further, more than 50% of the surface of the finished mould parts that consist of pores that breaks through the surface, have pores which are greater than the mean size of the  $\text{Si}_3\text{N}_4$  particles.

The shaping of mould parts from the silicon particles is preferably carried out at a pressure of below 200 MPa, and it is particularly preferred to carry out the shaping of the mould parts using vibration.

5 Tests with the use of  $\text{Si}_3\text{N}_4$  crucibles according to the present invention for directional solidification of molten silicon have shown that the solidified ingot did not, or to a very limited extent, stick to the walls of the crucibles. It was very surprising that crucibles having a high open porosity of between 40 and 60% by volume showed this property.

10

By providing the crucibles with a layer of silicon nitride powder with an average particle size of maximum  $50\mu\text{m}$ , any attachment of solidified silicon to the walls of the crucibles is avoided.

#### 15 **Short description of the figures**

Figure 1 shows the shape and dimensions of the crucible produced according to example 1.

#### **Detailed description of the Invention**

20

##### **Example 1**

A  $\text{Si}_3\text{N}_4$  crucible was produced according to the method of the present invention. Silicon powder having a particle size below  $75\mu\text{m}$  sold by Elkem ASA under the trademark SILGRAIN was filled into a mould having the shape  
25 and dimensions as shown in Figure 1. The silicon powder was compacted by vibration whereafter the crucible was nitrified at a temperature between 1105 and  $1380^\circ\text{C}$  in a vertical tube furnace until a conversion of silicon to  $\text{Si}_3\text{N}_4$  of 97% of theoretic conversion was achieved.

The produced crucible had an open porosity of 41.25% by volume and a  
30 density of  $1.85\text{ g/cm}^3$ .

The crucible according to the invention was used for directional solidification of silicon. The directional solidification was done by filling particulate silicon in the crucible. The crucible was then placed in a vertical tube furnace and argon

was supplied to the furnace in order to prevent oxidation of the crucible and of the molten silicon. The silicon in the crucible was melted at a temperature of 1500°C. The crucible was thereafter slowly lowered down through the furnace until the bottom of the crucible was positioned outside the hot zone. In this position the temperature was lowered 60°C pr. hour until the temperature reached 1375°C. The crucible was then cooled to room temperature. Upon examination it was found that the solidified silicon ingot was only affixed to the crucible on a few spots at the walls of the crucible where the open porosity was below 40% by volume and where the size of the pores was smaller than the  $\text{Si}_3\text{N}_4$  particles.

### Example 2

A crucible produced as described in example 1 was coated on its inside walls with  $\text{Si}_3\text{N}_4$  powder. The crucible was used for directional solidification of silicon according to the procedure described in example 1. Examination showed that the solidified silicon ingot was not affixed to the crucible.

**CLAIMS:**

1. Silicon nitride mould parts, particularly crucibles for use in connection with directional solidification and pulling of silicon single crystals,  
5 characterized in that the mould parts consist of  $\text{Si}_3\text{N}_4$  having a total open porosity between 40 and 60% by volume and where more than 50% of the pores in the surface of the mould parts have a size which is larger than the means size of the  $\text{Si}_3\text{N}_4$  particles.
- 10 2. Mould parts according to claim 1, characterized in that the mould parts are coated with silicon nitride particles having an average particle size of less than  $50\mu\text{m}$ .
- 15 3. Method for the production of silicon nitride mould parts, particularly crucibles for use in connection with directional solidification of silicon, where particulate silicon having a particle size of less than  $100\mu\text{m}$  is formed to a mould part and subjected to nitridation for conversion of the silicon particles to  $\text{Si}_3\text{N}_4$ , characterized in that the forming is carried out under such a pressure and with such a particle size distribution of the silicon particles that  
20 the finished silicon nitride mould part has an open porosity between 40 and 60% by volume and where more than 50% of the pores in the surface of the finished mould part are greater than the mean size of the  $\text{Si}_3\text{N}_4$  particles.
- 25 4. Method according to claim 3, characterized in that the shaping of the mould parts from the silicon particles is carried out at a pressure of below 200 Mpa.
5. Method according to claim 3, characterized in that the shaping of the mould parts are carried out using vibration.

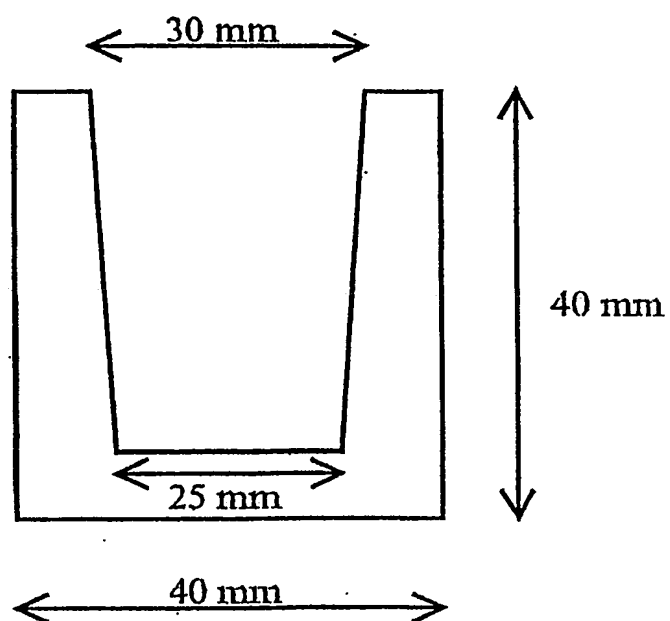


Figure 1

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 03/00274

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C30B 15/10, C04B 35/584

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C30B, C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4515755 A (SHUITSU MATSUO ET AL), 7 May 1985 (07.05.85), column 3, line 49 - line 51, abstract --	1-5
A	US 4888142 A (KENROU HAYASHI ET AL), 19 December 1989 (19.12.89), abstract --	1-5
A	DATABASE WPI Week 198450 Derwent Publications Ltd., London, GB; Class E36, AN 1984-308872 & JP 59162199 A (TEXAS INSTR INC) 13 September 1984 (1984-09-13) abstract --	1-5

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier application or patent but published on or after the international filing date
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- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI  Week 198301  Derwent Publications Ltd., London, GB;  Class E36, AN 1982-02540J,  &amp; JP 57188408 A (TOKYO SHIBAURA DENKI KK et al)  19 November 1982 (1982-11-19)  abstract</p> <p>--</p>	1-5
A	<p>DATABASE WPI  Week 199320  Derwent Publications Ltd., London, GB;  Class J04, AN 1993-164275  &amp; JP 5097571 A (TOSHIBA CERAMICS CO)  20 April 1993 (1993-04-20)  abstract</p> <p>--</p>	1-5
A	<p>PATENT ABSTRACTS OF JAPAN  vol. 008, no. 015  21 January 1984 (1984-01-21)  &amp; JP 58181793 A (TOSHIBA CERAMICS KK et al)  24 October 1983 (1983-10-24)  abstract</p> <p>--  -----</p>	1-5

# INTERNATIONAL SEARCH REPORT

Information on patent family members

06/09/03

International application No.

PCT/NO 03/00274

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